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MEMORANDUM FOR PR (In-House Publication)

FROM: PROI (TI) (STINFO) 05 Jun 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-123**
Harper, J., "Progress in Advanced Propellant Research"

NASA JPL-MSFC 11th Advances Space Propulsion Research Workshop **(Statement A)**
(Pasadena, CA, 31 May-02 Jun 00) **(Submission Deadline: 02 Jun 00)**

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ROBERT C. CORLEY (Date)
Senior Scientist (Propulsion)
Propulsion Directorate

Progress in Advanced Propellant Research

- **Cryogenic HEDM Solids**
- **Polynitrogen Compounds**
- **High Performance Monopropellants**
- **Hydrocarbon Fuels**

Capt. Jessica Harper
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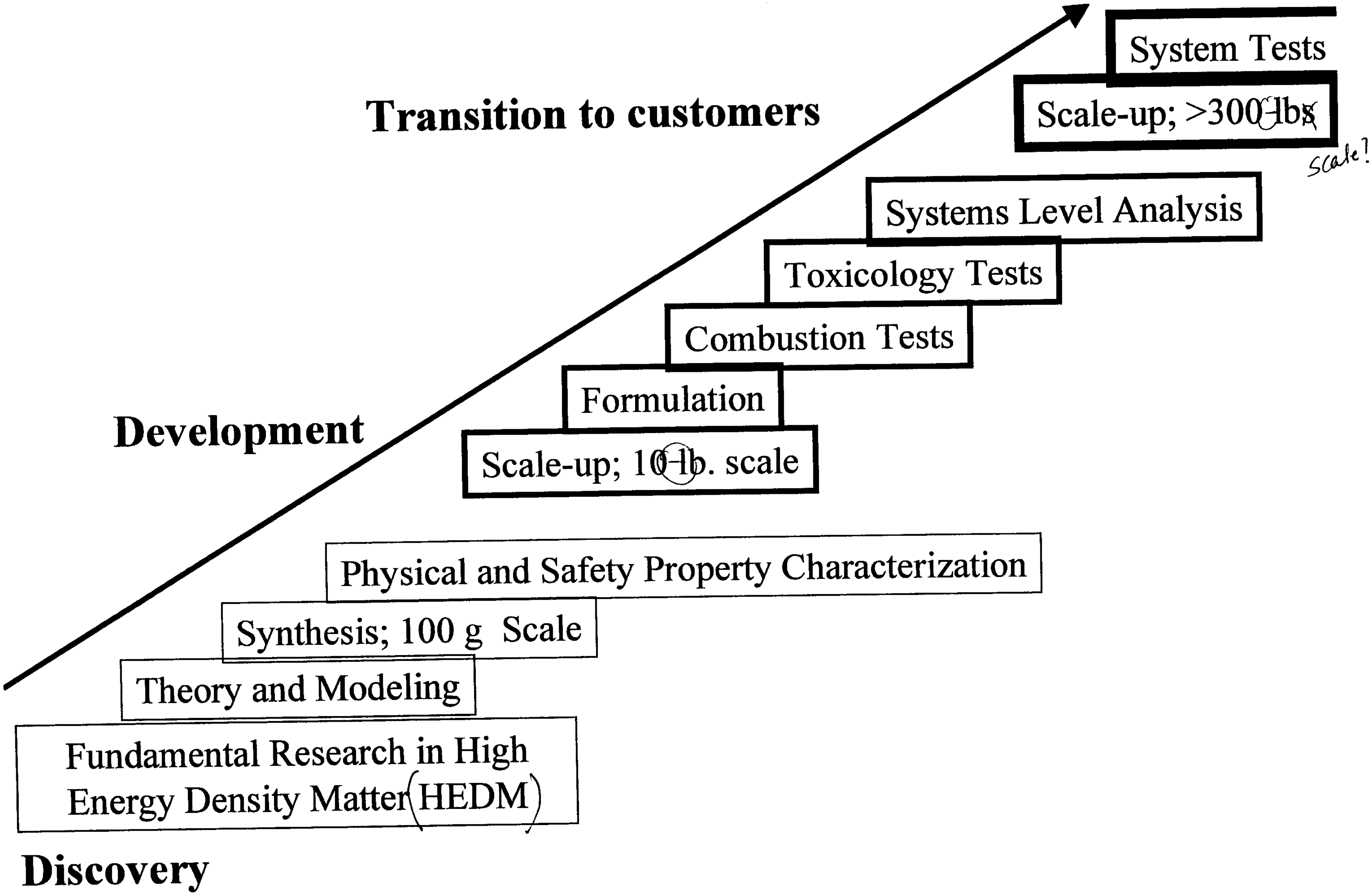
Propulsion Directorate mission includes discovery and development of envolutionary and revolutionary advances in propulsion systems

Distribution A: Unlimited Release
(I have added this to my cover slide. JH)

Technology Development Path



Cryogenic Solid HEDM Propellants

Use a solidified fuel or oxidizer as a storage medium for energetic additives, obtaining density and specific-impulse improvements

Depositing certain atomic or molecular species in solid hydrogen at 5% concentrations can increase specific impulse by more than 20%

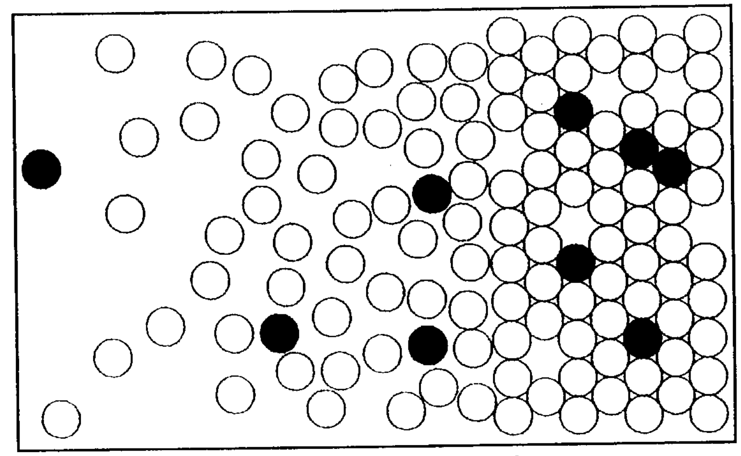
Vehicle	Propellant	Payload Mass (lb)	Payload (lb) With 10% Density Increase	Payload (lb) With 10% Isp Increase	Payload (lb) With 10% Increase in Both
Rockwell SSTO RLV	LH2/LOX (Isp = 455 s)	40,000	51,200 **(+28%)**	68,000 **(+70%)**	76,800 **(+92%)**

Large payload increases are achievable with modest density or specific impulse increases

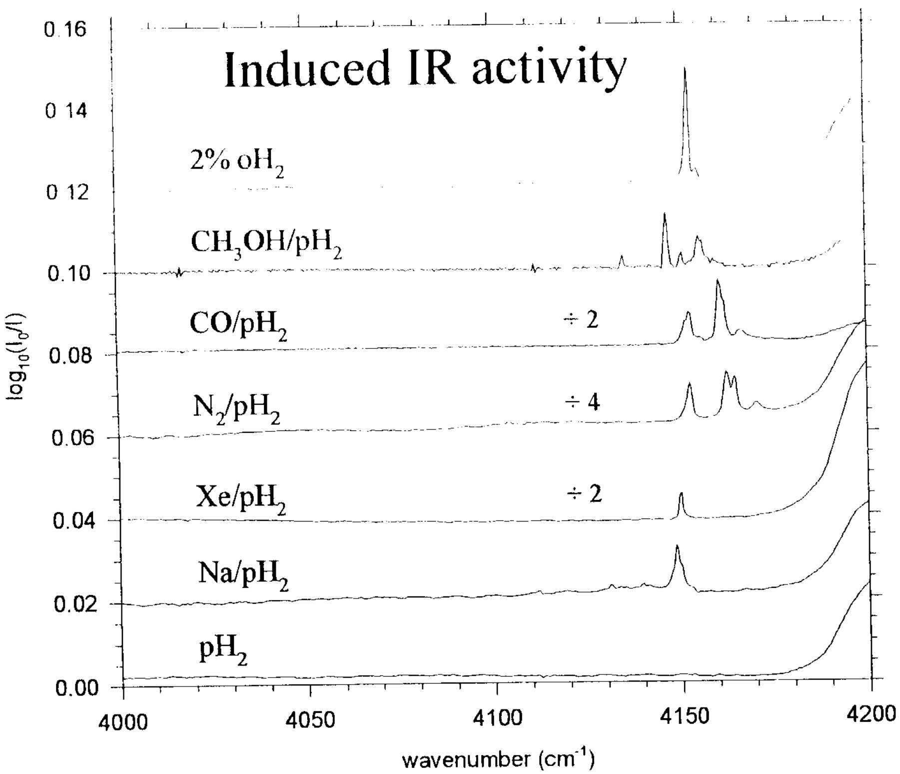
Cryogenic Solid HEDM Propellants

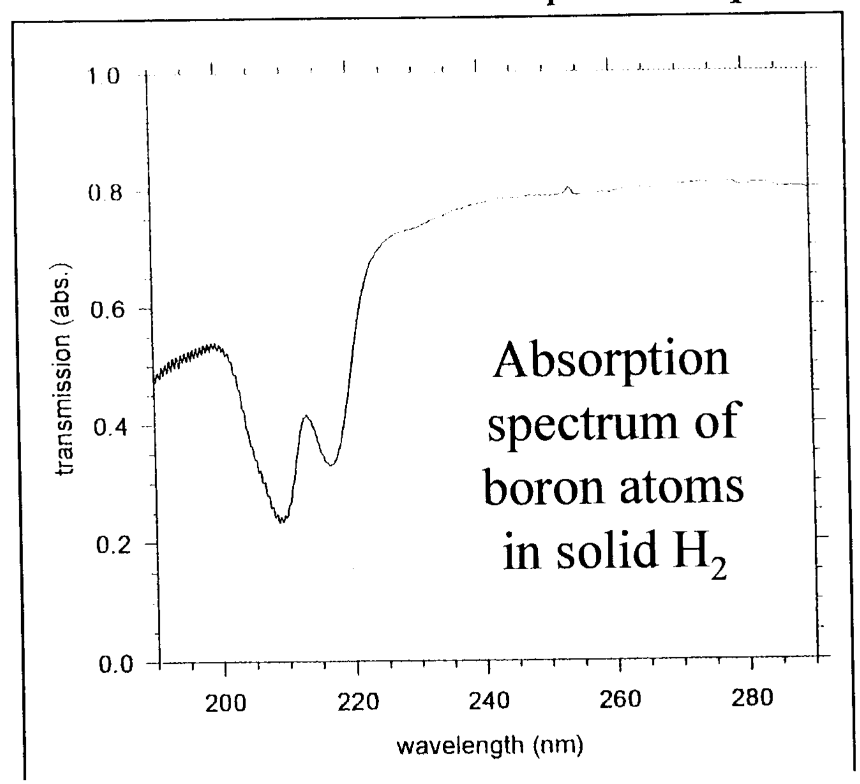
•***KEY ISSUE*** Develop methods to characterize thick cryogenic solids with high additive concentrations

•***APPROACH*** Investigate how direct dopant absorptions and the dopant-induced IR activity of H_2 relate to the type and concentration of HEDM additives.



Schematic of the deposition process





Cryogenic Solid HEDM Prospectus

BASELINE	Isp (sec)
Solid H2	389
5% ADDITIVE	
H	407
Be	452
B	472
C	469
Al	425
BH	449
CH	433
LiB	494
LiC	465
B2	492
BC2	482
B2C2	439

subscript?

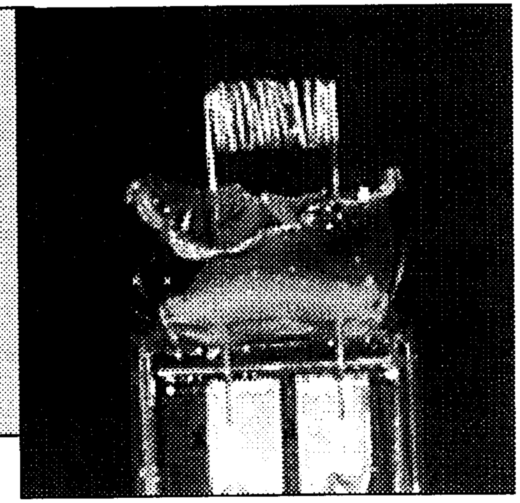
Can you subscript?

•*KEY ISSUE* Develop and characterize high-flux, robust, pure sources of desirable HEDM additives

•*APPROACH*

Boron filament source

Commercial aluminum deposition source



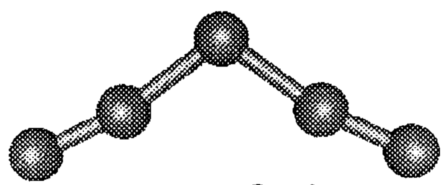
•*KEY ISSUE* Determine reactivity, diffusion, and recombination propensities to identify the most stable additives

italics?

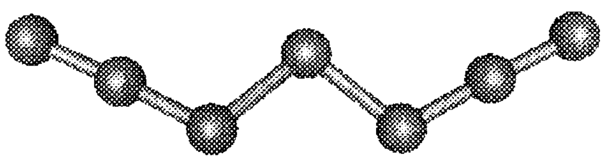
•APPROACH Simulations and experiments are yielding significant information about the chemical and thermal stabilities of doped solid H_2 and the dopant concentration limits.

Polynitrogen Calculations Led to Synthesis

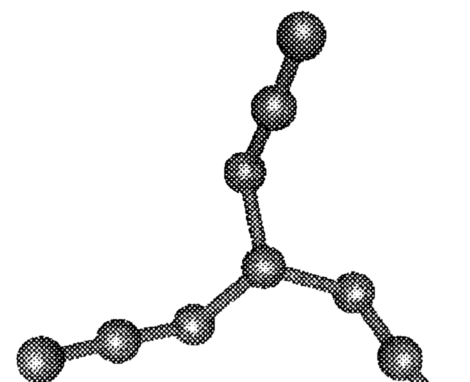
Program Objective: Synthesize and characterize new highly energetic polynitrogen compounds



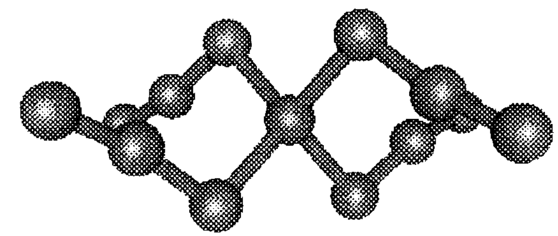
N_5^+ (C_{2v})



$N(N_3)_2^-$ (C_2)



$N(N_3)_3$ (C_3)

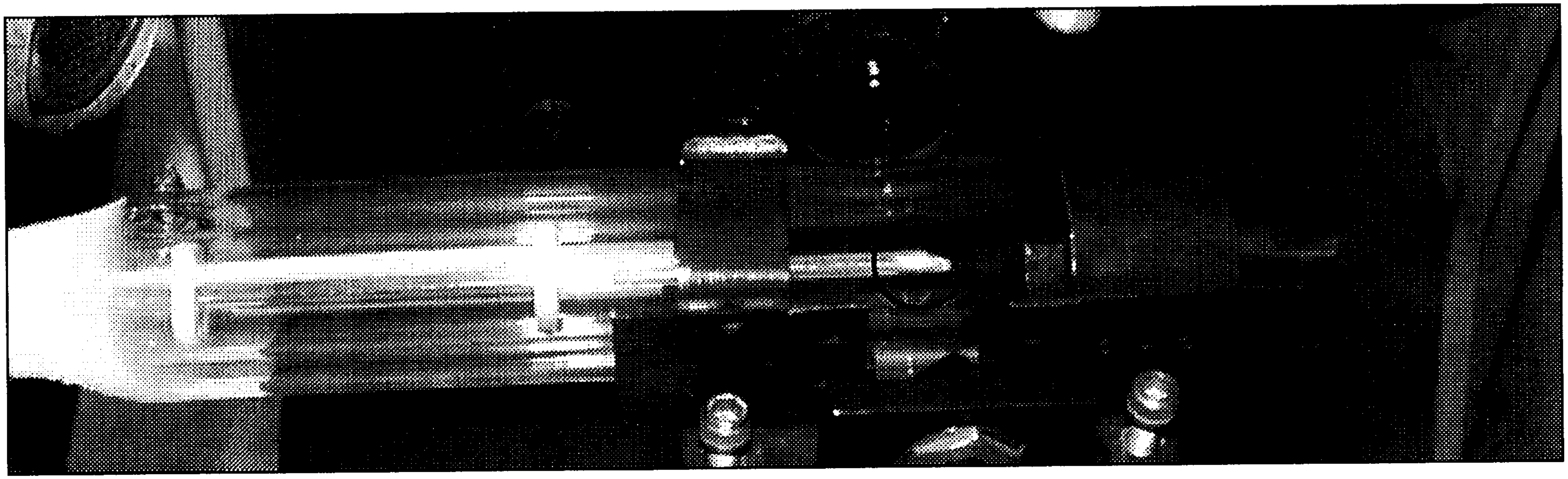


$N(N_3)_4^+$ (D_{2d})

- Calculations showed that the compounds depicted above are all stable, albeit to varying extents, and highly energetic
- Predicted measurable properties to help chemists identify what they made

This project is co-funded by DARPA and AFOSR

N_5^+ Salt in Low-Temperature Raman Spectrometer: Before and After Explosion



All Nitrogen Compound

Program Goal: Discover, characterize, and scale-up production of highly energetic all-nitrogen compounds for use as propellants or explosives.

Drs. Karl Christe, William Wilson, Jeffrey Sheehy, Jerry Boatz

Recent Accomplishments

- The N_5^+ cation is the first all-nitrogen compound to be prepared in bulk in over 100 years, and it is only the third known compound of this type
- Improved synthesis yields 5 g of N_5^+ salt in high purity at a fraction of the time of the previous synthesis
- A remarkably stable $N_5^+SbF_6^-$ salt was unambiguously identified by vibrational and NMR spectroscopy of unlabeled and ^{15}N-labeled N_5^+ in conjunction with quantum-chemical calculations
- Based on this initial success, the synthesis of additional new polynitrogen compounds is planned. A particular target is N_8, which could be formed as the ionic salt $N_5^+N_3^-$, or as a covalent compound such as azidopentazole

Significance

- Named one of "Chemistry's Top Five Achievements in 1999" by the American Chemical Society
- The feasibility of polynitrogen-based HEDM compounds has been demonstrated by the successful bulk synthesis of N_5^+
- Demonstrates synergy of calculations and experiment. Modeling and simulation were used to predict that the compound should exist, and computed spectra made it possible to identify and characterize the new N_5^+ compound
- Stable, neutral polynitrogens would be high performance monopropellants or explosives. N_8 as a monopropellant would have an Isp of 420 s, compared with hydrazine at 233 s. Clean propellant would have cost savings in handling, production, logistics, and disposal.

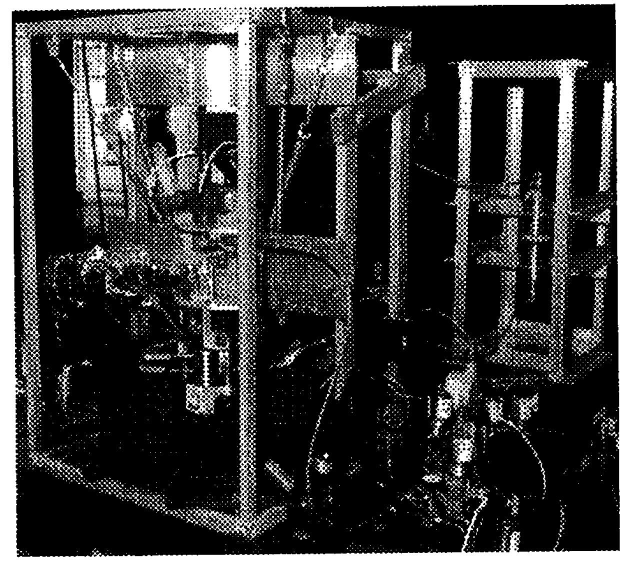
Monopropellant Development

Objective:
1) Develop monopropellants with higher performance and lower toxicity than SOTA (hydrazine). 2) Develop monopropellant to exceed bipropellant performance

Approach:
1) Synthesize and characterize energetic liquid salt ingredients

2) Formulate monopropellants with new ingredient

3) Combustion testing of formulations



Monopropellant Thrust Stand

Motives:
1) Enable AF satellite missions; AF aerospace vehicle; reduced size boost vehicle

2) Enable NASA small (< 100 kg) spacecraft and SSTO vehicles

3) Meet IHPRPT Phase II and III goals

(Economics of Space Transportation study (NASA-HQ) shows high energy density monoprops shrink vehicle size and cost for "generation-after-next" SSTO vehicles.)

High Performance, Reduced Toxicity Monopropellants

Properties	RK-618A	RK-315E	RK-100A	Hydrazine
Density Isp, % over SOTA (a)	+58	+61	+24	0.0
Chamber Temp. (Theoretical), K	2070	2083	1369	883
Carbon Content of Exhaust; (b)	none	none	none	none
Impact Sensitivity*, kg-cm (5 negatives)	>200	60	>200	>200
Friction Sensitivity, N (5 negatives)	318	300	>371	>371
NOL Card Gap (at 69 Cards)	negative	negative	negative	negative
Thermal Stability, %wt loss/48hr, 75°C	< 0.5	1.96	10.2	(< 0.1)
Melt Point, °C	5 (c)	<-22	-39	1

a: Theoretical, calculated with 300 psi chamber pressure, exhaust to vacuum, 50/1 expansion
b: as soot or solid carbon (by theoretical computation)
c: by DSC; melt transition was broad, melt peak reported
*: For reference, n-propylnitrate had an impact sensitivity of 8 kg-cm

RK-618 and RK-315 Propellants Display Acceptable Safety/Sensitivity Properties For Continued Development

Advanced Monopropellants

Dr. Tom Hawkins, Dr. Greg Drake, Adam Brand,
Milton McKay, Dr. Ismail Ismail

Recent Accomplishments

- Thruster test of low-toxicity monopropellant at National Hover Test Facility at PR-w and at Atlantic Research Corporation. Determined catalyst behavior, and C*, exhaust products.
- Synthesized and tested a dozen new ingredients. Identified a compound for scale-up.
- Toxicology assessment, completed by AFRL/HE (Dr. Dave Mattie), shows these monoprops 6X less oral toxicity than hydrazine. Very low dermal irritation.
- Gelled monopropellant developed.
- Numerous collaborators--Primex, ARC, NASA/GRC, small businesses...

Significance

- Technology transfer and evaluation in commercial industry of monopropellant with theoretical density impulse increase of 61% over hydrazine. Verifies in-house thruster test results.
- Theoretical monopropellant performance with new ingredients equals or exceeds current bipropellant (NTO/MMH) systems.
- Verifies that these propellants will have cost savings in handling, production, logistics, and disposal. Environmentally benign as well.
- Increases range of operability for some systems.
- Sharing resources will advance the program at a faster rate.

Liquid Hydrocarbon Fuels

Objective:

Develop cost-effective high energy, high density liquid hydrocarbons to enhance or replace RP and JP fuels.

Approach:

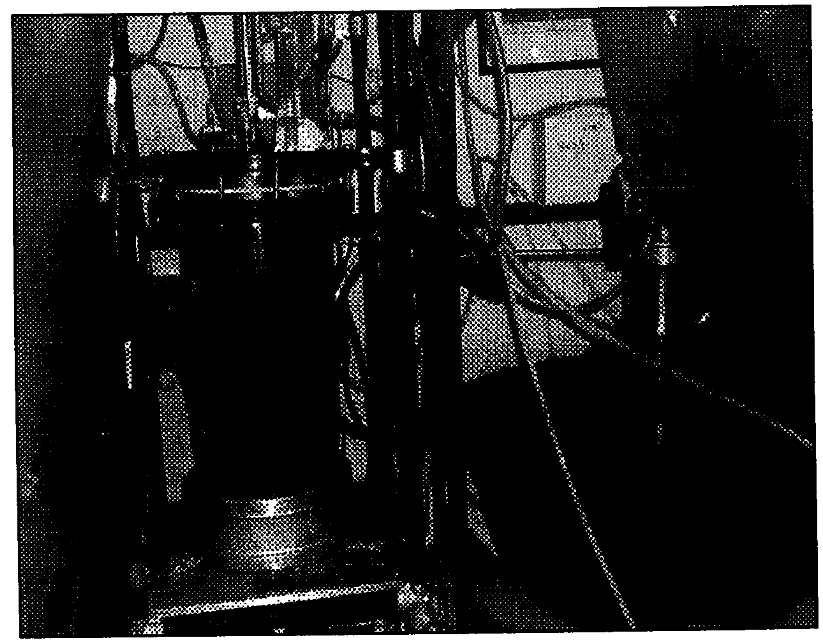
1) HEDM synthesis; novel molecules; property testing
2) 10 lb. scale-up of promising candidates; combustion testing
3) Scale up to ton quantities through business collaborations

Motives:

1) Enable new AF missions (air breathers or rockets)

2) NASA Access to Space concepts--supported with \$200K in FY99; \$50K likely in FY00

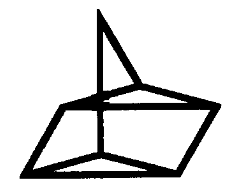
3) Meet IHPRPT Phase II and III goals



30L scale-up equipment at AFRL

Theoretical Performance Comparison of Energetic Hydrocarbons

Hydrocarbons	H/C ratio	Density g/ml	Calc.ΔHf (Kcal/mole)	Calc.Isp sec
RP-1	1.9	0.80	-	300.0
Quad	1.14	0.98	72.2	307.0
BCP	1.33	0.85	76.1	312.5
AFRL-1	1.2	0.77	64.0	311.3
AFRL-2	1.25	0.87	73.4	307.2
AFRL-3	1.0	0.93	123.6	307.2
AFRL-4	1.0	-	129.6	321.4



Energetic Hydrocarbon Fuels

Dr. Suresh Suri, Mike Tinnirello, Paul Jones

Recent Accomplishments

- Four energetic hydrocarbons (BCP, AFRL-1, quadricyclane, 1,7 octadiyne) passed physical property, material compatibility, and thermal stability tests.
- Improved bicyclopropylidene (BCP) bench-scale synthesis to produce ~8 lbs.
- Delivered three energetic hydrocarbons (BCP, quadricyclane, 1,7 octadiyne) to NASA/MSFC for combustion testing.
- Initial tests by AFRL/HE determined quad and BCP to have low toxicity.
- BCP shown to be hypergolic with N_2O_4, IRFNA and possibly H_2O_2.
- Synthesized AFRL-3.

Significance

- Candidates have passed initial hurdles. All are suitable for combustion testing.
- First time BCP produced in these quantities. Material now available for testing.
- Combustion results will indicate candidates potential for further scale-up.
- Verifies that these propellants can be handled in the same way as RP-1.
- BCP could be lower toxicity replacement for MMH. May enable new design of systems that burn nonhypergolic propellants.

Summary

- Cryogenic solid HEDM doped with energetic atoms and molecules is being pursued with special attention on how to produce and measure 5% dopants in solid H_2.

- Synthesis of the N_5 cation was a breakthrough towards making a high energy all nitrogen propellant.

- Low toxicity high performance monopropellants offer dramatic improvements over hydrazine,

- Fruitful collaboration with NASA/MSFC; will test fire BCP, 1,7-octadiyne, quadricyclane in 100-lb. thruster; Hydrocarbon program has products close to transition,